

Effect of Temperature and Pressure on Equilibrium Relations between Gases and Liquids

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Fundamental Design of High Pressure Equipment Involving Paraffin Hydrocarbons

II. Fugacities of Paraffin Hydrocarbons

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IT IS customary to use the vapor pressure as a quantitative measure of the escaping tendency of a liquid. The vapor pressure of a liquid is defined as the pressure of the pure vapor in equilibrium with the pure liquid. In the case of mixtures it is customary to assume Dalton's law of partial pressures which is dependent upon the ideal gas laws, and to use as the escaping tendency of a liquid component its partial vapor pressure which is equal to the partial pressure of the same component in the vapor phase under equilibrium conditions. It is also customary to assume that the vapor pressure of a liquid is entirely dependent upon the temperature and independent of pressure. These assumptions may lead to large errors.

EFFECT OF PRESSURE ON VAPOR PRESSURE OF A PURE LIQUID

If a semi-permeable diaphragm is placed between a pure liquid and its vapor so that only the vapor is allowed to pass through the diaphragm, the pressure upon the liquid phase may be varied at will independently of that upon the vapor phase. If, under these conditions, the pressure upon the liquid phase is increased, the increase in the escaping tendency of the liquid might be considered as the increase in the vapor pressure of the liquid or the increase in the pressure on the vapor phase necessary to maintain equilibrium conditions. The computation of this increase in vapor pressure of the pure liquid brought about by an increase in external pressures is a classical problem (1, 3, 4), usually solved by placing the increase in potential or free energy of the liquid phase equal to the increase in potential of the vapor phase. Using F as a symbol for this potential according to the usage of Lewis and Randall,

$$d\bar{F}_L = d\bar{F}_V$$

$\bar{F}_L$ = potential or free energy of unit mass of liquid

$\bar{F}_V$ = potential or free energy of unit mass of vapor

$$d\bar{F}_L = v dP = d\bar{F}_V = V dp$$

v = volume of unit mass of liquid

V = volume of unit mass of vapor

P = total pressure on liquid phase

p = pressure on vapor phase in equilibrium with liquid phase or vapor pressure of liquid

$$V dp = v dP$$

$$\frac{dp}{dP} = \frac{v}{V} \quad (1)$$

If the vapor is assumed to be an ideal gas,

$$pV = RT$$

$$V = \frac{RT}{p}$$

$$\frac{dp}{p} = \frac{v dP}{RT} \quad (2)$$

The vapor pressure of the pure liquid, p_p , when under a total pressure, P , is different from the normal vapor pressure, p_n , and may be calculated by integrating Equation 2 between limits as indicated below:

$$\ln p_P = \ln p_n + \frac{1}{RT} \int_{p_n}^P v dP$$

If the vapor is not assumed to be an ideal gas, the deviations from the ideal may be properly considered by use of the z function shown in Figure 4 of Part I. Since

$$z = \frac{pV}{RT}$$

$$V = z \frac{RT}{p}$$

and the equation to be integrated becomes

$$\int_{p_n}^{p_P} z \frac{dp}{p} = \frac{1}{RT} \int_{p_n}^P v dP \quad (3)$$

The results of the integration of Equation 3 should give accurately the vapor pressure of a pure liquid as a function of the total pressure upon the liquid. In order to apply the results of such calculations to hydrocarbon mixtures, it is necessary to assume the validity of Raoult's law for the liquid phase, and for the vapor phase either Dalton's law or the more general assumption that the total pressure is equal to the summation of the partial pressures of the components in the

vapor phase when such partial pressures are determined as the pressure that would be exerted by each component when occupying the total volume of the vapor phase at the same temperature. These assumptions when applied to paraffin hydrocarbons are probably within the limits of accuracy required for engineering work. But Equation 3 was not used for determining the equilibrium conditions between liquid and vapor because of the inconvenience of integrating both sides of the equation, and because the integration requires the use of extrapolated P-V-T values.

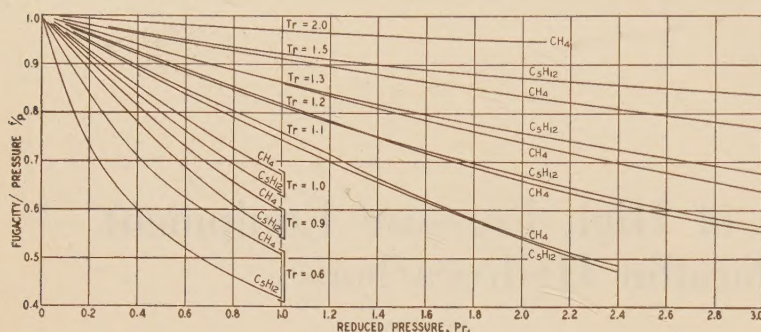


FIGURE 1. FUGACITY OF VAPOR

The more convenient method of using the fugacities of the liquid and vapor hydrocarbons with the assumption of ideal solutions was chosen, although it may, or may not, be more accurate than the use of Equation 3 in the manner indicated.

The assumption that the liquid phase is an ideal solution is more or less equivalent to the assumption of Raoult's law and the use of the corrected vapor pressure, and the assumption that the vapor phase is an ideal solution may be more or less equivalent to the assumption that the total pressure is equal to the sum of the partial pressures. It will be necessary to determine the P-V-T relationship for mixtures of hydrocarbons in order to determine which assumption fits the experimental data more closely. This work is now in progress.

FUGACITIES OF PARAFFIN HYDROCARBONS

Lewis (2, 3) has proposed the fugacity as a general measure of the escaping tendency of a component from a phase. The fugacity is equal to the vapor pressure when the vapor is an ideal gas and may in general be regarded as an ideal or corrected vapor pressure.

FUGACITY OF VAPORS. The isothermal relationship between fugacity and total pressure is represented by the equation (3, 5),

$$\left(\frac{\partial \ln f}{\partial P}\right)_T = \frac{V}{RT} \quad (4)$$

If the P-V-T relations of a gas and its fugacity at one pressure are known, the fugacities at other pressures may be determined by integration of this equation, using the z function from Figure 4 of Part I as before:

$$V = z \frac{RT}{P}$$

$$RT(d \ln f) = RT \frac{z dP}{P} \quad (5)$$

$$\int_0^{f_P} d \ln f = \int_0^P z(d \ln P) \quad (6)$$

Since the fugacity is equal to the pressure when the pressure is zero, the lower limit of the left-hand side of Equation 6 may be omitted, and the equation may be written:

$$\ln f_P = \int_0^P z(d \ln P) \quad (7)$$

The fugacity at various pressures may be determined conveniently by graphical integration of this expression in Equation 7. The results of these computations on methane and pentane are given in Figure 1, where the ratio $\frac{f}{P}$ is plotted as a function of the reduced pressure for constant reduced temperatures.

FUGACITY OF LIQUIDS. Under equilibrium conditions the fugacity of a component in the liquid phase equals its fugacity in the vapor phase. The fugacity of a pure liquid under its vapor pressure, therefore, is equal to the fugacity of the vapor when under the vapor pressure. If the vapor is an ideal gas, the fugacity of the liquid is equal to its vapor pressure. Frequently it is desired to use the fugacity of the liquid under a total pressure which is different from the normal vapor pressure of the liquid at that temperature. For such purposes it is necessary to compute the effect of pressure on the fugacity of the liquid at constant temperature. This may be done by use of the equation,

$$RT(d \ln f) = v dP$$

where v = molal volume of liquid
 P = total pressure on liquid

In most cases the compressibility of the liquid is almost negligible, so that v may be assumed constant. Under these conditions the integrated equation takes the form:

$$\ln \frac{f_P}{f_{p_n}} = \frac{v}{RT} (P - p_n)$$

When the difference between the total pressure, P , and the normal vapor pressure, p_n , is less than one-tenth of the absolute temperature, this effect of pressure on the fugacity of the liquid may be neglected.

The following calculation of the effect of total pressure on the fugacity of liquid normal pentane is given as an indication of the method and importance of making this correction. The ratio between the fugacity of normal pentane at 80° F. under a pressure of 510 pounds per square inch and the fugacity of liquid pentane at 80° F., under its normal vapor pressure of 10.3 pounds per square inch, is computed in the following manner: Assuming the liquid incompressible, v is constant at 1.88 cubic feet per pound mole, then

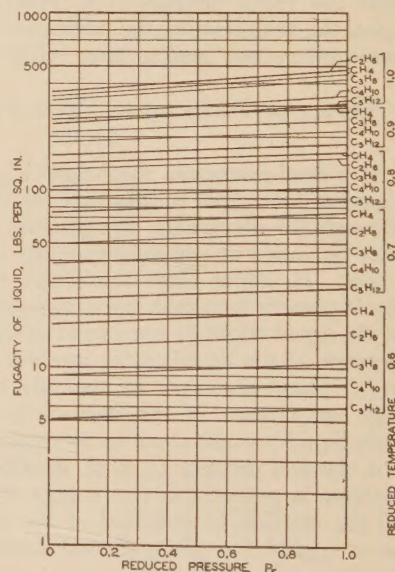


FIGURE 2. FUGACITY OF LIQUID

$$\ln \left(\frac{f_{510}}{f_{10.3}} \right) = \frac{1.88 \times 499.7}{10.71 \times 540} = 0.1627$$

$$\frac{f_{510}}{f_{10.3}} = 1.177$$

Therefore the neglect of the effect of pressure on the fugacity of normal pentane would in this case introduce an error of about 18 per cent. Since these conditions of temperature and pressure are frequently encountered in the absorption of natural gasoline, it is necessary to consider the effect of pressure on the fugacity of liquid hydrocarbons. These calculations have been made and are presented in Figure 2, in which the fugacity of the liquid hydrocarbons is plotted as a

function of the reduced pressure for constant reduced temperatures.

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III. Equilibria between Liquid and Vapor Solutions of Paraffin Hydrocarbons

MOTT SOUDERS, JR., C. W. SELHEIMER, AND GEORGE GRANGER BROWN

THE equilibrium relationship between vapor and liquid hydrocarbons is of major importance in practically all operations of the natural gasoline industry. At low pressures of not over 40 or 60 pounds the simple rules for approximating equilibrium relationships may be used without introducing serious error in engineering calculations.

LAWS OF EQUILIBRIA

HENRY'S LAW. In 1802 Henry (2) suggested the relationship which now bears his name. In effect, Henry's law may be stated as follows: Unit initial mass of a liquid solvent absorbs a mass of gas which is proportional to the pressure of the gas. Mathematically this may be stated as

$$\frac{x}{1-x} = Kp \quad (1)$$

where x = mole fraction of gas in liquid phase
 K = a constant for each temperature
 p = pressure of gas

DALTON'S LAW. Dalton (1), while reviewing Henry's data, noted that the solubility of each gas of a mixture was proportional to the product of the concentration of the individual gas and the total pressure. On this basis Dalton advanced his law of partial pressures: The pressure of an individual gas in a gaseous mixture is equal to the product of the total pressure and the concentration of the individual gas.

Combining these two relations, we have the mathematical statement:

$$\frac{x}{1-x} = KP_y \quad (2)$$

where P = total pressure on gas phase
 y = mole fraction of individual gaseous component in gaseous phase

In general, it appears that Henry's law is valid when the concentration of the dissolved gas in the liquid phase is small and when the deviation of the gas from the ideal gas laws is slight. All available experimental data which confirm Henry's law were obtained under these conditions.

RAOULT'S LAW. Much later, Raoult (4) suggested that the partial vapor pressure exerted by a component in a liquid solution is equal to the product of the mole fraction of the component and the vapor pressure of the pure component at the temperature of the solution. Mathematically,

$$p_n x = p p$$

where p_n = normal vapor pressure of pure component at temperature of solution
 $p p$ = partial vapor pressure of component in solution

Combining this relationship with Dalton's law, Raoult's law becomes

$$p_n x = P y \quad (3)$$

In general, Raoult's law has been observed to apply to

solutions of paraffin hydrocarbons in a fairly satisfactory manner over wide ranges of composition when the temperature and pressure are such that the vapor of each component does not deviate greatly from the ideal gas laws at either the vapor pressure of the pure component or at the total pressure. The similarity between Raoult's law and Henry's law at low concentrations of the dissolved components in the liquid phase may be shown by expanding Equation 2 (Henry) to the series,

$$\frac{1}{K} (x + x^2 + x^3 + \dots) = P y$$

If x is small, so that the terms with exponents greater than 1 may be neglected, Henry's law becomes

$$\frac{x}{K} = P y$$

which is identical with Raoult's equation if

$$p_n = \frac{1}{K}$$

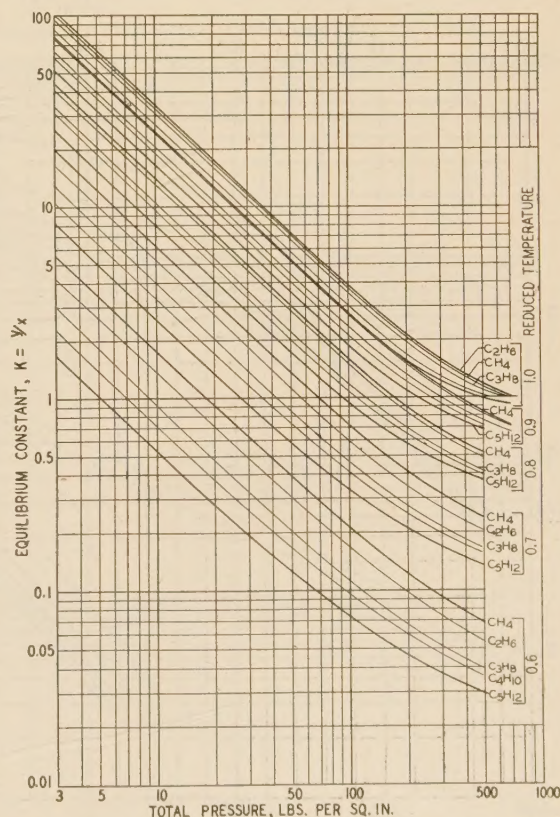


FIGURE 1. EQUILIBRIUM CONSTANT AS FUNCTION OF PRESSURE

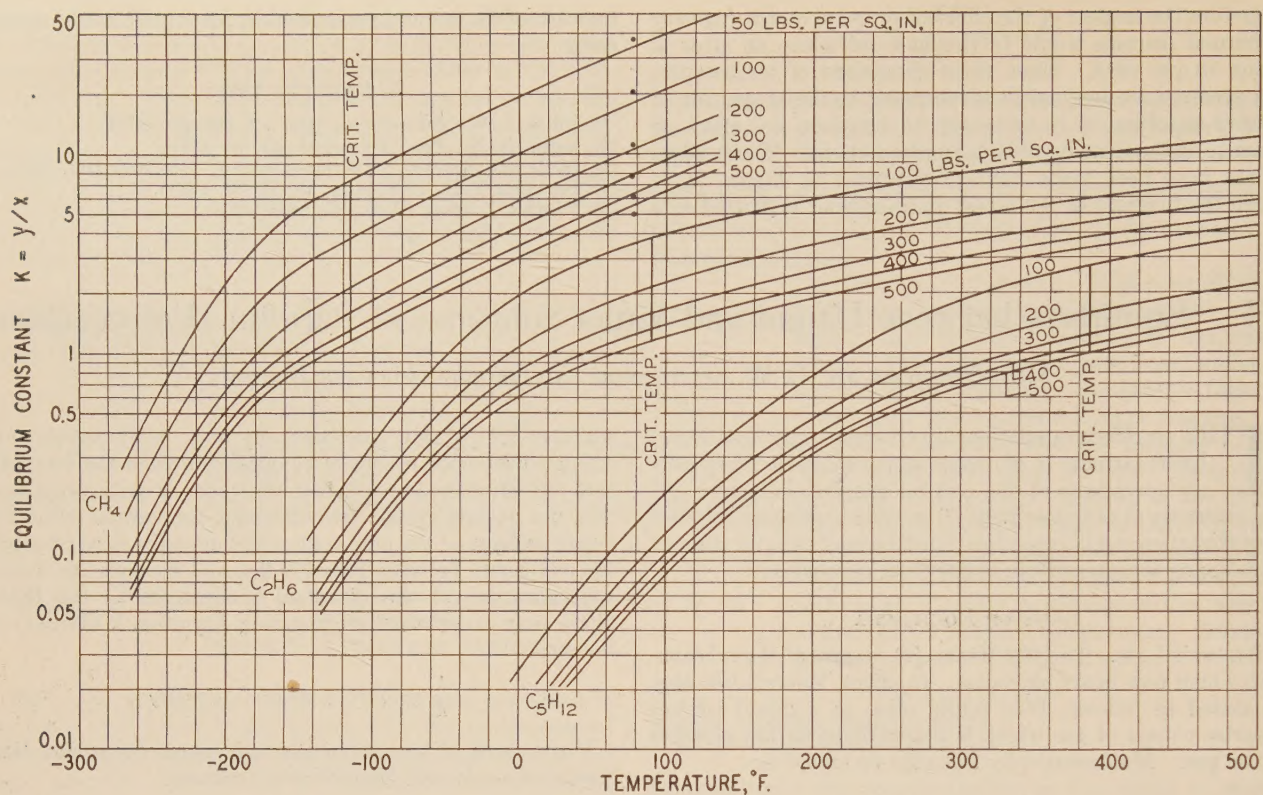


FIGURE 2. EQUILIBRIUM CONSTANT AS FUNCTION OF TEMPERATURE

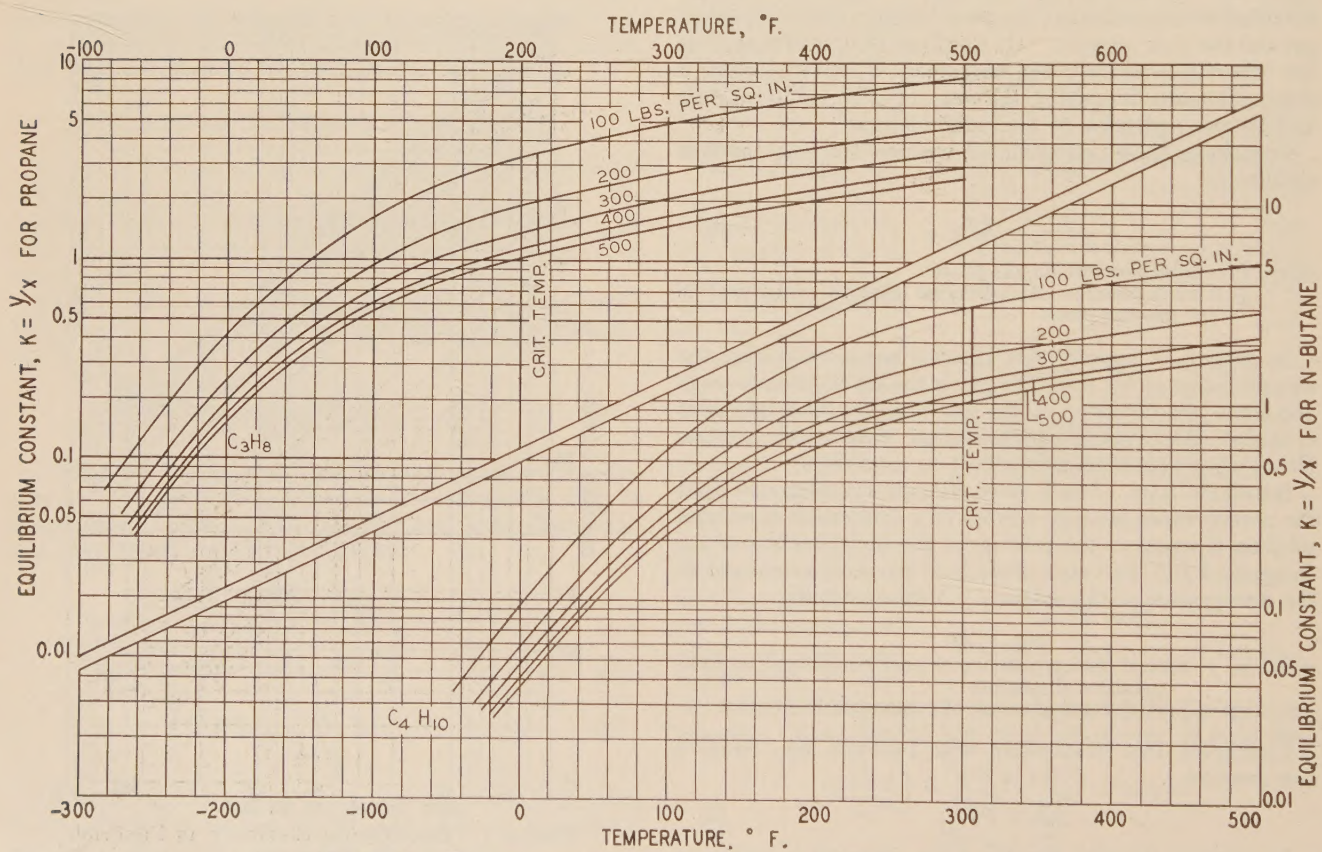


FIGURE 3. EQUILIBRIUM CONSTANT AS FUNCTION OF TEMPERATURE

These simple rules for approximating the equilibrium conditions between liquid and vapor introduce serious errors at higher pressure or under conditions where the ideal gas laws do not apply.

THE IDEAL SOLUTION

"The ideal solution is one in which the fugacity of each component is proportional to the mole fraction of that component at every pressure and temperature" (3). In mixtures of chemically similar liquids where the forces between unlike molecules are nearly the same as the forces between like molecules, according to the laws of probability the number of molecules of any component leaving the liquid should be proportional to the mole fraction of that component. Solutions of the liquid paraffin hydrocarbons appear to conform to the ideal solution in a reasonably satisfactory manner (5). No serious error is to be expected if the vapor mixtures are also considered ideal solutions, for in the vapor state the molecules are more widely separated and are allowed more nearly independent action than in the liquid phase. If both liquid and vapor mixtures are regarded as ideal solutions, the fugacity of each component is equal to the product of the mole fraction and the fugacity of the pure component in a like phase at the same temperature and pressure, and the general equation for equilibrium becomes

$$f_L x = f_v y \quad (4)$$

f_L = fugacity of pure component as liquid at same temperature and total pressure

f_v = fugacity of pure component as vapor at same temperature and total pressure

The errors introduced by these assumptions have been found to be much less than those involved in the assumption of Raoult's and Dalton's laws and are apparently within the limits required of modern engineering practice. Further experimental work in determining accurately the equilibrium between liquid and vapor solutions, now in process, must be completed before the accuracy of these relationships can be determined in a satisfactory manner.

VAPOR-LIQUID EQUILIBRIUM CONSTANT

For purposes of convenience the ratio between the mole fraction in the vapor phase and the mole fraction in the liquid phase under equilibrium conditions for any component is defined as the equilibrium constant for that component at the corresponding temperature and pressure. Mathematically this equilibrium constant, K , may be expressed by the equation:

$$K = \frac{y}{x} = \frac{f_L}{f_v} \quad (5)$$

Since f_L and f_v for each component are functions solely of the temperature and total pressure, the values for the equilibrium constant, K , may be plotted as a function of temperature and pressure for each component. These values for K are plotted as a function of total pressure at constant reduced temperatures in Figure 1, and as a function of temperature for constant total pressures in Figures 2 and 3.

In the entire absence of reliable data on the solubility of gases as a function of temperature, it is suggested that these plots as extrapolated above the critical temperature be used until such data can be obtained.

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Through the courtesy of P. K. Frolich and L. F. Marek of the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology, satisfactory data were made available on the solubility of methane in pentane and other paraffin hydrocarbons at 25° C. and at pressures up to 2000 pounds per square inch. The equilibrium constants computed from these experimental data are indicated in Figure 2 for purposes of comparison.

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